The Electrolytic Formation of Persulphate. Part III. Study of the Electrodes.

By Ryoichi MATSUDA and Teruichi NISHIMORI.

(Received June 2nd, 1937.)

The anode plays a very important part in electrolytic oxidation. Selection of the anode material, its treatment and other conditions are limited especially in the case of electrolysis which involves strong acid solutions as in the present one. Platinum is the anode material which can be used exclusively in such a case, and an alternative to it has been long sought in vain.

The influence of igniting a Pt-anode previously to electrolysis was studied in Part II[1] of this investigation, and several other treatments of the anode are subsequently dealt with in this paper. The length of the Pt-wire cathode is also changed to see the influence of the cathodic current density, but nothing remarkable is found to take place.

Experiment 1. Influence of the Cathodic Current Density. The anode consists of a spiral of Pt-wire which is 0.05 cm. in diameter and 20.7 cm. in length, and the cathode also of Pt-wire as thick as the anode, which is wound spirally against the wall of the electrolytic vessel. Three different lengths of the cathode are employed, i.e., 20, 45, and 107 cm. 130 c.c. of 15 N sulphuric acid are electrolysed with these electrodes at 15°C. without diaphragm. Current efficiency (to be abbreviated as C.E. hereafter) for different current densities is shown in Table 1 and Fig. 1 and 2, the same amount of electricity being supplied in each case.

Table 1. Current Efficiency with the Length of the Cathode varied, the Electrolyte being 15 N Sulphuric Acid.

The length of the cathode \ The current (amp.)		0.163	0.325	0.650	0.975	1.30	1.95	2.60
The Caro's acid C.E.	20 cm.	22.8%	34.2	38.0	34.3	30.4	28.4	27.0
	45	20.0	24.1	24.1	23.5	24.8	25.5	24.1
	107	4.8	33.4	31.5	28.4	25.8	19.2	15.7
The total C.E.	20	31.0	49.1	65.6	74.8	77.7	76.0	75.6
	45	25.5	40.0	58.7	67.3	71.7	74.0	65.5
	107	14.1	38.5	57.1	70.0	70.9	70.9	70.1

(1) This Bulletin, **11** (1936), 650.

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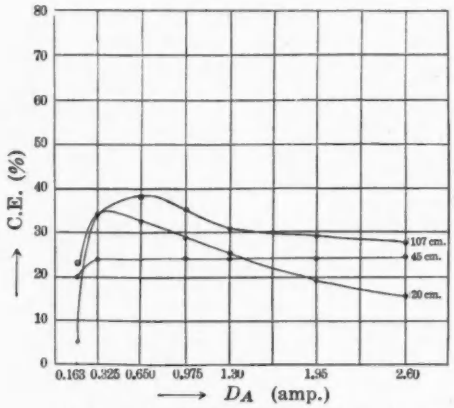

Fig. 1. Caro's Acid C.E. with Various Lengths of the Cathode.

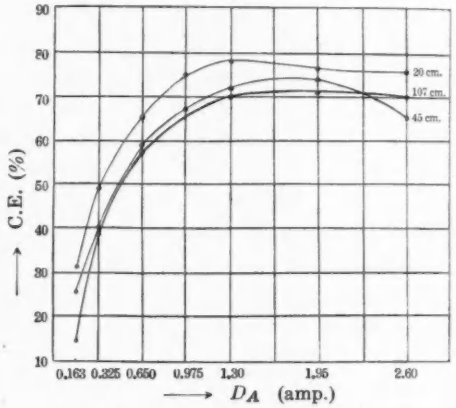

Fig. 2. The Total C.E. with Various Lengths of the Cathode.

The total C.E. is greater, the shorter the cathode: therefore a longer cathode is evidently more effective in reducing the peroxidic anodic products in spite of its smaller cathodic current density, because the influence of the cathode on C.E. probably consists merely in reducing the anodic products.

The greater the total C.E., in this experiment, the smaller the C.E. as to Caro's acid, which was the case also in Experiment 3 of Part II in which 15 N sulphate solutions containing various amounts of ammonium sulphate and sulphuric acid were electrolysed. In the latter case the fact was explained by means of the difference of sulphuric acid concentration. In the present case, however, the reason must be attributed to the condition of the cathode or something connected with it, because both the electrolyte and the anode are similar. Although it is not clearly known why, it seems likely that firstly Caro's acid is formed in greater amount when the cathode is longer, and secondly Caro's acid is reduced more easily than persulphuric acid when it comes near, or in contact with, the cathode irrespective of the magnitude of the cathodic current density.

Experiment 2. PbO_2-anode. PbO_2-anode was studied by several investigators, e.g., its preparation from lead nitrate solution by Y. Kato and K. Koizumi[2] and that from lead tartrate solution by G. Angel and H. Mellquist[3]. Both of these methods are examined in their adoptability

(2) *J. Electrochem. Assoc. Japan*, **2** (1934), 309.
(3) *Z. Elektrochem.*, **40** (1934), 702.

for the present purpose. Lead dioxide is deposited electrolytically on a Pt-anode from lead nitrate solution, whose compositions are varied as follows: 5 to 39 g. $Pb(NO_3)_2$, 1 to 10 c.c. conc. HNO_3, 0 to 1 g. gelatine, 90 to 95 c.c. water.

The Pt-anode is the same as used in Experiment 1 and the cathode is one of 45 cm. in length described above. The current is varied 0.04 to 3.0 amp., the temperature 50° to 80°C., and the time of electrolysis 1 to 30 minutes. It is found that the deposition of lead dioxide is the hardest, the most uniform and adherent when the solution contains 39.0 g. $Pb(NO_3)_2$, 1.0 c.c. conc. HNO_3, 90 c.c. water and 1 g. gelatine, and the temperature 77°C., the current 0.5 amp., and the time of electrolysis 30 minutes. A solution which is 3 and 4 N respectively as regards ammonium sulphate and sulphuric acid is electrolysed without diaphragm at 15°C. with the PbO_2-anode prepared under the best conditions as mentioned above. Three different intensities of current, 1.30, 1.95 and 2.60 amp., are applied for the electrolysis, the amount of electricity being the same, i.e., 1170 coulombs in each case. The total C.E. remains 3.0 to 3.1% for all the three intensities of current. When 15 N sulphuric acid is electrolysed under the same conditions as above, the total C.E. is even less than 3.0%. The PbO_2-anode prepared from lead nitrate solution under the other conditions is proved unavailable for the electrolysis, since the PbO_2-layer comes off partly or entirely during electrolysis.

Angel and Mellquist[3] say that they succeeded in preparing a PbO_2-anode by depositing lead dioxide on iron, steel or copper from lead tartrate solution, and the deposition of the same on platinum is here examined. A 13% KOH solution containing 17.7 g. lead tartrate in 100 c.c. is electrolysed at 14° to 17°C. by a current of 1.30 amp. for 15 minutes with the same anode and cathode as used in the previous case, and lead dioxide is deposited on the anode. While a solution which is 3 and 4 N respectively as regards ammonium sulphate and sulphuric acid is being electrolysed with the PbO_2-anode thus prepared and a Pt-cathode by a current of 1.30 amp. at 15°C., it is found that lead dioxide comes off entirely from the Pt-base.

Experiment 3. Carbon-anode. An anode is made of gas carbon which is of rectangular section 4 mm.^{2} and 3 cm. in length. The cathode is the Pt-one as used in previous cases. Three electrolyses are tested with these electrodes at 15°C. without diaphragm: 10 N sulphuric acid with a current of 2.6 amp., 6 N ammonium sulphate solution with 0.163 amp., and 6 N ammonium sulphate solution containing ammonia with 0.163 amp. The

carbon-anode is found, in each of these cases, partly to disintegrate, therefore its use is not promising.

Experiment 4. Various Treatments of the Pt-anode. 130 c.c. of 15 N sulphuric acid are electrolysed without diaphragm for 30 minutes at 15°C. with an anodic current density of 20 amp./dm.^{2} Both the anode and cathode which is 45 cm. long are as described in Experiment 1, and the former, however, is subjected, immediately before use, to various heat treatments as follows.

When hydrogen and acetylene are used as the fuel for the treatments, each of these is led to a blast lamp and burned with air whose amount is so controlled as to keep the temperature of the Pt-anode which is put in the blast just to white heat. The temperatures to which the anode is heated are kept as near as possible throughout the treatments.

Table 2. Various Treatments of the Pt-Anode.

	Caro's acid C.E.	The Total C.E.
Coal gas flame[1]	24.1%	58.7%
Hydrogen flame	17.0 18.9 mean 18.0	50.0 46.1 mean 48.1
Acetylene flame	16.1 16.2 mean 16.2	63.0 60.5 mean 61.8
D.C. (downwards)	18.3 19.5 mean 18.9	50.2 58.7 mean 54.5
D.C. (upwards)	17.4 17.7 mean 17.6	53.5 54.4 mean 54.0
A.C.	20.9 21.1 mean 21.0	63.8 64.4 mean 64.1

Though it is not clear what takes place in the Pt-anode as the result of its heat treatments, more or less differences of C.E. are seen to occur according to the kind of treatment. Among the three kinds of flame

acetylene gives the best total C.E., hydrogen the poorest, and coal gas comes between them. Therefore the presence of hydrocarbon in the combustible gas or its combustion seems favourable to improve the anode activity.

The electrical treatment in which D.C. is flowed from the top of the anode to its lower end is denoted in the table as D.C. (downwards) and the reversed case as D.C. (upwards). There is no considerable difference between the influences of these two on C.E. The A.C. treatment, however, is superior to the D.C. treatment in increasing C.E. and gives the greatest total C.E. of all.

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Note on a Theory of the Expanded Film.

By Kyozo ARIYAMA.

(Received June 5th, 1937.)

Although numerous theories have been proposed, the nature of the expanded film appears still undecided. In a recent paper Langmuir[1] tried to explain the phenomena and proposed the equation of state of the following form

$$(F-F_0)(a-a_0) = kT, \qquad (1)$$

where F is the two dimensional gas pressure, a the surface area for a molecule, T the absolute temperature, k the Boltzmann's constant. F_0 and a_0 appear as constants to be determined by experiments. With suitable choice of F_0 and a_0, he shows that equation (1) represents the equation of state fairly well. However he does not discuss the nature of these constants, and considers that the presence of a kink in the observed F–a curve is due to the sudden appearance of micelles. Why the micelles, if any, should appear suddenly is still a subject of theoretical speculation.

I would like to propose the following explanation for the sudden appearance of the expanded state. According to the theory of Langevin-Weiss, an ensemble of molecules with permanent magnetic moment or

(1) *J. Chem. Phys.*, **1** (1933), 756.

electric moment can exhibit the 'Ferromagnetic state', and there is a sharp critical temperature at which the transition from paramagnetic to ferromagnetic state takes place. Born[2] applied this theory to the explanation of the existence of the sharp critical temperature at which the anisotropy of a liquid crystal disappears. According to Born, there is the following relation between the electric moment μ of the molecule and the critical temperature T_c

$$\mu^2 = \frac{9kT_c}{4\pi N}, \qquad (2)$$

where N is the number of the molecules in a cubic centimeter.

Now in the case of solids for which the 'ferromagnetic state' is possible, the number of molecules N is an almost fixed quantity, so that there is only one critical temperature. If on the other hand, we have a substance whose density can be varied so that N takes on continuously changing values, then there will be corresponding continuous changes in the critical temperature T_c. In other words for any given temperature, there is one and only one density at which the 'ferromagnetic state' can set in for any molecules having dipole moments.

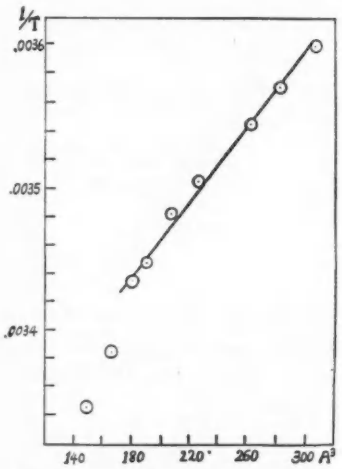

Fig. 1. The Relation between the Reciprocal of Temperature and the Critical Molecular Volume for Films of Myristic Acid.

Let us consider for a moment that the 'ferromagnetic state' is also possible for two dimensional states, and assume that Born's argument applies here in unmodified form. Then the critical volume V_c of the molecule for any given temperature T will be given by

$$V_c = \frac{1}{N} = \frac{4\pi}{9}\frac{\mu^2}{kT}. \qquad (3)$$

Thus it is expected that V_c should vary inversely as the temperature. This can be tested by the experimental data on myristic acid films.[3] Figure 1

(2) *Ann. Physik*, **55** (1918), 222.

(3) Adam and Jessop, *Proc. Roy. Soc.* (London), A, **112** (1926), 362.

shows the experimental relation. We see that the theoretical conclusion holds fairly well except for the two lowest points at which the discrepancy becomes quite marked.

Assuming equation (3) to be correct, we can calculate the electric moment μ of the myristic acid. The value found from Figure 1 is 2.5×10^{-18} e.s.u. No direct measurement of the electric moment of myristic acid seems to have been reported; but Meyer[4] has calculated that rotation within the carboxyl group should cause a variation of moment with temperature, the lower limit and the upper limit being 1.1×10^{-18} and 3.5×10^{-18} respectively. Thus the value 2.5×10^{-18} seems quite reasonable. The point of view described here does not seem to conflict with various experimental facts of the expanded films.

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Corrections to the papers published in Vol. 12, No. 1.

Page	Line	Read
35	21	in the case of $SrCl_2$, however, for K_2SO_4, $MgCl_2$, $BaCl_2$, and Na_2SO_4
42	2	$e^{\sqrt{a^2+k_2^2}x-ax_1}$
43	equation (9)	$\Gamma = -\frac{c}{kT}\left[\frac{\epsilon^2}{4D}+\frac{\epsilon^2}{4D}\left(\frac{d^2+2da}{a^2}\right)-\frac{\epsilon^2}{2D'}\left(\frac{da+d^2}{a'^2}\right)\right]$
44	left hand side of equation (2)	$-\left(\frac{\partial\tau}{\partial c_1}\right)c_2$

(4) *Z. physik. Chem.*, B, **8** (1930), 27.

Studies on Amino-Acids and Related Compounds. Part X. Electrolytic Oxidation of Aspartic Acid and Malonic Acid.*

By Yoshitaro TAKAYAMA and Saburo MIDUNO.

(Received June 19th, 1937.)

In a previous paper,[1] it was briefly described that the electrolytic oxidation of aspartic acid is rather more complicated in mechanism than that of glutamic acid, although the two compounds are analogous in their structure. In the present paper, the course of oxidation of aspartic acid will be further discussed in its details.

By oxidizing aspartic acid with hydrogen peroxide, Dakin[2] obtained formic acid, acetic acid and acetaldehyde together with a little malonic acid. Langheld[3] obtained acetaldehyde on heating aspartic acid with sodium hypochlorite, and considered malonic acid semialdehyde to be an intermediate product.

In the present experiments, aspartic acid was oxidized with lead peroxide anode in sulphuric acid solution under two different conditions in temperature, one at 35° and the other at about 100°. Malonic acid, which can be presumed to be one of the reaction products in the above oxidation, was also oxidized just in the same way.

In the experiment carried out at 35°, formic acid (10.8 mol%), malonic acid (1.4%), succinic acid (small quantity), ammonia and carbon dioxide were isolated as the oxidation products of aspartic acid. In the same condition, formic acid and carbon dioxide were isolated from malonic acid.

In the case of 100°, the aspect of reaction is somewhat different. Volatile products formed during the electrolysis were slowly distilled off at this temperature and further oxidation of these products was thus prevented. Acetaldehyde (4.1 mol%), formic acid (28.14%), succinic acid (0.36%), ammonia and carbon dioxide were isolated from the oxidation products of aspartic acid. Formic acid (35.2%) together with a little formaldehyde was isolated from those of malonic acid.[4]

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* Translated by the authors from *J. Chem. Soc. Japan*, **56** (1935), 1460.

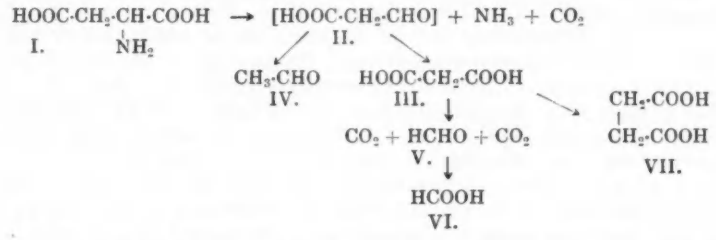
(1) Part VII, this Bulletin, **8** (1933), 215.

(2) H. D. Dakin, *J. Biol. Chem.*, **5** (1909), 409.

(3) K. L. Langheld, *Ber.*, **42** (1909), 2370.

(4) E. Durand, *Chem. Zentr.*, **1903**, II, 968.

From these results, the mechanism of the electrolytic oxidation of aspartic acid and malonic acid may be represented as follows.



The first stage of the oxidation of aspartic acid (I) is doubtless the formation of malonic acid semialdehyde (II). This unstable aldehyde immediately produces malonic acid (III) by further oxidation. Another change occurs without oxidation, and the aldehyde, at the temperature of 100°, losing carbon dioxide,[5] turns into acetaldehyde (IV). Further oxidation of malonic acid leads to the formation of formic acid (VI) through formaldehyde (V). While the formation of succinic acid (VII), as Fichter[6] pointed out, is due to the electrolytic oxidation of malonic acid.

Experimental.

I. Electrolytic oxidation of aspartic acid.

Aspartic acid (Kahlbaum) (Found: N, 10.52. Calculated for $C_4H_7O_4N$: N, 10.53%). Apparatus. In the case of 35°, an undivided cell, electrodes (4 cm. × 5 cm.): lead peroxide—lead. In the case of 98–99°, a cylindrical glass vessel (diameter 3 cm., height 12 cm.) provided with a rubber stopper carrying two electrodes, a thermometer and a dropping funnel. A delivery tube connecting to a receiver through a condenser was fused to the cell. During the electrolysis, the volatile oxidation products were distilled into the receiver which was cooled in ice. Electrodes: lead peroxide anode (6 cm. × 7.5 cm.), lead cathode (6 cm. × 4 cm.).

Experiment at 35°. Two cells (each of which contained 6.653 g. or 1/10 mol of aspartic acid in 120 c.c. of N H_2SO_4) were connected in series and immersed in a thermostat of 35°. C.D.: 2 amp./dm.^{2} Current quantities 8.146 F./mol. After the electrolysis the nitrogen distribution (NH_3-N/total N) in the electrolyzate was determined (73.9%) and the main bulk was subjected to steam distillation. In the distillate, no substance giving aldehydic reaction was found.

Volatile acid (formic acid). The distillate was titrated with N/10NaOH (106.5 c.c., 10.8 mol%). The resulting salt was converted into lead salt and analysed. Lead formate (Found: Pb, 69.32. Calculated for $(HCO_2)_2Pb$: Pb, 69.71%).

(5) A. Wohl, *Ber.*, **33** (1900), 2763.

(6) Fr. Fichter and J. Heer, *Helv. Chim. Acta*, **18** (1935), 704.

Non-volatile acids (*malonic and succinic acids*). The residue of the steam distillation was concentrated and extracted with ether. The first part of the ethereal extract yielded a little quantity of crystals on evaporation of the solvent. The crystalline acid, recrystallized from water, melted at 183°. It was identified as succinic acid by the determination of acid equivalent, mixed melting point test and colour reaction of resorcine—sulphuric acid test. The last part of the ethereal extract was evaporated, leaving an oil which slowly crystallized (0.07 g., 1.4 mol% as malonic acid). The crystals, when recrystallized from dilute alcohol, melted at 132–133° and no depression of melting point was observed when mixed with a pure sample of malonic acid. 0.0414 g. of the acid required 7.89 c.c. of N/10NaOH. Calculated for malonic acid ($C_3H_4O_4$): 7.96 c.c. The malonic acid was also identified as barium salt. The salt was dissolved in hot water and reprecipitated with alcohol. Barium malonate[7] (Found: Ba, 52.93. Calculated for $C_3H_2O_4Ba \cdot H_2O$: Ba, 53.38%).

Volatile base (*ammonia*). The residual solution of above extraction was distilled under reduced pressure with an excess of barium hydroxide. The volatile base was collected in dilute hydrochloric acid. Hydrochloride 1.4 g. Ammonium chloroplatinate (Found: Pt, 43.69. Calculated for $(NH_4)_2PtCl_6$: Pt, 43.96%).

After above treatments, the solution was freed from SO_4'' and $Ba^{\cdot\cdot}$ as usual. Crystalline acid (0.55 g.) was isolated which was identified to be unchanged aspartic acid by the ninhydrin reaction and determination of nitrogen (N, 10.48%).

Experiment at 98–99°. Aspartic acid (3.326 g. × 2, 1/20 mol) was dissolved in N H_2SO_4 (40 c.c. × 2) and electrolyzed in two undivided cells connected in series. The cells were placed in an air thermostat of 98–99°. C.D.: 2 amp./dm.^{2} Current quantities: 8.148 F./mol. The distribution of nitrogen of the electrolyzate: NH_3-N/total N = 73.93%. During the electrolysis, loss of water in the cell caused by distillation was compensated continuously through the dropping funnel.

Volatile substances (*acetaldehyde, formic acid*). Volatile acid, distilled during electrolysis, required 125.1 c.c. of N/10 NaOH; ditto, obtained by steam distillation after electrolysis, 13.9 c.c. of N/10 NaOH; total: 139.0 c.c. of N/10 NaOH, or 28.1 mol% to aspartic acid. The volatile acid was identified to be formic acid by the reaction with mercuric chloride and silver nitrate as well as by the analysis of its lead salt. Lead formate (Found: Pb, 69.47. Calculated for $(CHO_2)_2Pb$: Pb, 69.71%).

Amount of the aldehyde in the distillate was estimated by the titration of the neutralized distillate with bisulphite solution: 2.021 millimol (4.10 mol%) or 0.0890 g. of acetaldehyde. Acetaldehyde-*p*-nitrophenylhydrazone, m.p. 125–126° (Found: N, 23.56. Calculated for $C_8H_9N_3O_2$: N, 23.46%). It showed no depression of melting point when mixed with a specimen of *p*-nitrophenylhydrazone prepared from pure acetaldehyde (Kahlbaum).

Non-volatile acid (*succinic acid*). The residual solution was extracted thoroughly with ether. The ethereal solution was evaporated, leaving crystalline acid which was recrystallized from water. It melted at 183° and was identified as succinic acid by the mixed melting point test. 21 mg. (0.36 mol%) of succinic acid from 1/20 mol aspartic acid (current quantities: 6.17 F./mol; NH_3-N/total N = 41%). The presence of malonic acid could not be confirmed.

(7) C. Coutelle, *J. prakt. Chem.*, **73** (1906), 73.

Volatile base (*ammonia*). Hydrochloride 0.9 g. Chloroplatinate (Found: Pt, 43.79. Calculated for $(NH_4)_2PtCl_6$: Pt, 43.96%).

After the removal of the substances described above, unchanged aspartic acid (0.144 g.) was recovered from the residue (Found: N, 10.38. Calculated for $C_4H_7O_4N$: N, 10.53%).

II. **Electrolytic oxidation of Malonic Acid.**

Experiment at 35°. Malonic acid (Kahlbaum, 1.3005 g. × 2, 1/40 mol) was dissolved in N H_2SO_4 (120 c.c. × 2) and electrolyzed in two cells connected in series. C.D.: 2 amp./dm.^{2} Current quantities 3.07 F./mol. The electrolyzate was treated in the same manner as in the case of aspartic acid.

Volatile acid (*formic acid*). It required 16.70 c.c. of N/10 NaOH, corresponding to 13.4 mol%, and the acid was identified as formic acid by the reaction with silver nitrate and mercuric chloride and also by the crystalline form of the lead salt.

Experiment at 97°. Malonic acid (2.601 g. × 2, 1/20 mol) was dissolved in N H_2SO_4 (40 c.c. × 2) and electrolyzed under the same condition as in the case of aspartic acid. Current quantities: 8.25 F./mol.

Volatile substances (*formic acid, formaldehyde*). The acid, distilled during the electrolysis (A) required 103.16 c.c. of N/10 NaOH; ditto, obtained by steam distillation after electrolysis (B), 73.00 c.c. of N/10 NaOH; total: 176.16 c.c. of N/10 NaOH, 35.2 mol%. Lead formate (Found: Pb, 70.03% (A), 69.89% (B). Calculated for $(CHO_2)_2Pb$: Pb, 69.71%).

The volatile neutral part of the distillate gave fuchsin reaction and Rimini's reaction, and produced silver mirror. The formaldehyde was determined by the method of G. Romijn: 4.835 mg. (0.32 mol%).

Non-volatile acid (*succinic acid*). The residue of steam distillation was extracted with ether. The crystals (m.p. 183°, 7.1 mg.) obtained from the ethereal solution were identified as succinic acid by mixed melting point test, as well as by the colour reaction of resorcine-sulphuric acid test.

In conclusion, the authors wish to express their sincere thanks to Prof. K. Matsubara for kind inspection of this paper.

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Studies on Amino-Acids and Related Compounds. Part XI. The Formation of Aldehydes by the Electrolytic Oxidation of α-Amino-Acids.*

By Yoshitaro TAKAYAMA, Takeshi HARADA, and Saburo MIDUNO.

(Received June 19th, 1937.)

In connection with biological oxidation, numerous attempts have been made to elucidate the mechanism of oxidation of α-amino-acids, and several compounds[1] (ketonic acid, imino-acid etc.) have been suggested as the intermediate products of their oxidation.

It was experimentally confirmed that by chemical oxidation amino-acids always produce the next lower aldehydes at the first stage of their oxidation. By electrolytic oxidation of amino-acids in sulphuric acid with platinum anodes, Fichter[2] obtained a little of aldehyde together with other oxidation products, and concluded that the aldehyde is the first oxidation product.

As described in Part VII,[3] when amino-acids were oxidized electrolytically with lead peroxide anode, the aldehyde was found in only a few case, and the author mentioned that aldehyde may be formed but soon further oxidized, and also that the course of reaction may proceed as follows:

$$\begin{array}{l} \mathrm{R{\cdot}CH{\cdot}COOH} \longrightarrow \mathrm{R{\cdot}CHO} + \mathrm{NH_3} + \mathrm{CO_2} \\ \quad\downarrow \mathrm{NH_2} \qquad\qquad \downarrow \\ \quad \text{Melanin} \qquad \mathrm{R{\cdot}COOH} \end{array}$$

where R denotes the radicals of aliphatic, aromatic and heterocyclic compounds.

In Part X,[4] it was proved that malonic acid semialdehyde was the first oxidation product of aspartic acid, and the present experiments were undertaken in the same manner to confirm the aldehyde formation from other amino-acids. By removing the oxidation products as quickly as possible from the electrolyzates to prevent further oxidation, aldehydes were successfully obtained in comparatively abundant quantity from four amino-acids.

* Translated by the authors from *J. Chem. Soc. Japan*, **57** (1936), 449.

(1) Bergel and Bolz, *Z. physiol. Chem.*, **215** (1933), 25; Bergel, *ibid.*, **233** (1934), 66.

(2) Fichter and Schmid, *Helv. Chim. Acta*, **3** (1920), 704.

(3) Takayama, this Bulletin, **8** (1933), 213.

(4) Takayama, this Bulletin, **12** (1937), 333.

On oxidizing glycine, alanine and leucine, Fichter[5] obtained formaldehyde, formic acid, ammonia, amines and carbon dioxide from glycine; acetaldehyde, acetic acid, formaldehyde, formic acid and ammonia, as well as carbon dioxide from alanine; isovaleraldehyde, isovaleric acid, isobutyric acid, acetone and acetic acid from leucine.

In the present experiments, alanine was oxidized in dilute sulphuric acid with lead peroxide anode at 35°, and acetic acid, ammonia and carbon dioxide were isolated, but no aldehyde was found. On the contrary, when alanine was oxidized in the same manner as aspartic acid at about 100°, the volatile oxidation products being distilled off during electrolysis, acetaldehyde (36.5%[6] as *p*-nitrophenylhydrazone) together with acetic acid (17.8%), ammonia and carbon dioxide was obtained.

Even in the experiment at 35°, when the volatile oxidation products were driven into absorption bottles by bubbling air through the cell, other conditions being the same, acetaldehyde could be abundantly separated in the form of *p*-nitrophenylhydrazone and dimedon-derivative. From this fact it was concluded that the absence of the aldehyde in the former experiments was due to further oxidation.

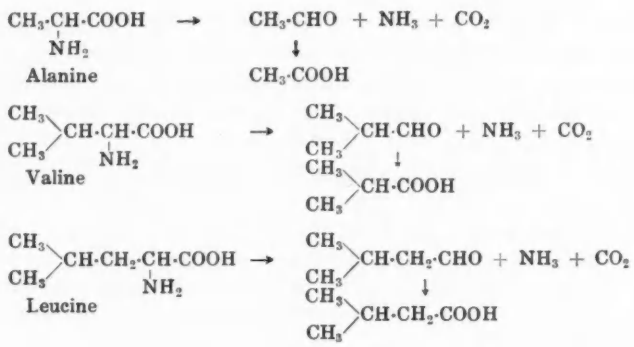
Glycine was oxidized in the same manner and formaldehyde (16.6%) together with formic acid (4.85%) was obtained. Ammonia, methyl-, dimethyl- and trimethyl-amines were isolated as volatile bases. These amines probably resulted from the action of formaldehyde with ammonia.[7] Likewise, valine gave isobutyraldehyde (32.1%) and isobutyric acid (27.5%) on its oxidation.

Fichter[5] mentioned that the electrolytic oxidation of leucine is vigorous and proceeds on even to acetone. This fact was observed also in Part VII.[3] Leucine was oxidized in the same way as alanine at about 100°, and the distillate thus obtained consisted of oily and aqueous layers. The former almost exclusively consisted of isovaleraldehyde (yield 53–56%). The latter contained isovaleric acid (yield 20–22%), but not the lower fatty acids.

From these results, the mechanism of the electrolytic oxidation described above may be represented as follows:

$$\begin{array}{lcl} CH_2\cdot COOH & \rightarrow & H\cdot CHO + NH_3 + CO_2 \\ \downarrow & & \downarrow \\ NH_2 & & \\ \text{Glycine} & & H\cdot COOH \end{array}$$

(5) Fichter and Kuhn, *Helv. Chim. Acta*, **7** (1924), 164.
(6) The percentages in this paper were expressed in molar per cent.
(7) Plöchl, *Ber.*, **21** (1888), 2117.



Thus, from the experiments on glycine, alanine, valine, leucine and aspartic acid,[4] it may be concluded that the first stage of the electrolytic oxidation of α-amino-acid is the aldehyde formation, and that the general expression described before will represent the course of the electrolytic oxidation of α-amino-acid. Some of these reactions may be applied to industrial purposes.[8]

Experimental.

I. Electrolytic oxidation of alanine.

Experiment at 35°. Alanine (Kahlbaum) (Found: N, 15.83. Calculated for $C_3H_7O_2N$: N, 15.73%). Alanine (8.911 g., 1/10 mol) was dissolved in N H_2SO_4 (120 c.c. × 2) and electrolyzed in two undivided cells connected in series, under following conditions. Cell: similar as described in Part IV.[9] Electrodes (4 cm. × 5 cm.): lead peroxide anode and lead cathode. C.D.: 2 amp./dm.^{2} Current quantities: 7.923 F./mol. The distribution of nitrogen in the electrolyzate after electrolysis: NH_3-N/total N = 96.6%.

During the electrolysis, evolved gas was led to ice-cooled washing bottles containing water to catch both acidic and neutral substances. The aqueous solution in the above bottle gave no aldehydic reaction. The electrolyzate was subjected to steam distillation. The distillate was separated into neutral and acidic parts. The former gave no aldehydic reaction, and the latter was converted into sodium salt.

Volatile acid (*acetic acid*). The sodium salt (4.34 g.) of volatile acid was identified as acetate by acetic ester test and by iodine-lanthanum reaction. Silver acetate (Found: Ag, 64.72. Calculated for $C_2H_3O_2Ag$: Ag, 64.64%).

Volatile base (*ammonia*). After the removal of the volatile acid from the electrolyzate, the residue was distilled with an excess of barium hydroxide under reduced pressure. The volatile base was converted into hydrochloride. It was identified as ammonia. Ammonium chloroplatinate (Found: Pt, 43.68. Calculated for $(NH_4)_2PtCl_6$: Pt, 43.96%).

(8) Japanese patent 110,640.

(9) This Bulletin, **8** (1933), 175.

Only unchanged alanine was recovered from the residue of the above base.

Experiment at 96°. Alanine (2.227 g., 1/40 mol) was dissolved in N H_2SO_4 (40 c.c.) and electrolyzed under the following conditions. Apparatus: the same apparatus as described in Part X.[9] During the electrolysis, the volatile oxidation product was distilled into a receiver which was cooled in ice. Temperature: 96°. Electrodes: lead peroxide anode (6 cm. × 7.5 cm.), lead cathode (6 cm. × 4 cm.). C.D.: 2 amp./dm.^{2} Current quantities: 8.09 F./mol. 3 volts. The distribution of nitrogen in the electrolyzate: NH_3-N/total N = 98.11%. The electrolyzate was treated in the same way as in the case of 35°.

Volatile neutral solution (acetaldehyde). Both the distillate caught in the ice-cooled water and the distillate obtained from the electrolyzate by steam distillation were combined, neutralized and separated into neutral and acidic parts by distillation. Neutral part gave fuchsin-sulphurous acid reaction and silver mirror. *p*-Nitrophenylhydrazone (1.6 g., 36.5%), recrystallized from carbon tetrachloride, gave m.p. 126°. It was identified as acetaldehyde-*p*-nitrophenylhydrazone (m.p. 126°) by mixed melting point test and by nitrogen determination (Found: N, 23.77. Calculated for $C_8H_9N_3O_2$: N, 23.46%).

Volatile acid (acetic acid). The acidic part described above required 43.70 c.c. of N/10 NaOH. That is 17.8% to decomposed alanine. Silver acetate (Found: Ag, 64.72. Calculated for $C_2H_3O_2Ag$: Ag, 64.64%).

Volatile base (ammonia). It was treated in the same manner as in the case of 35°. Hydrochloride 1.1 g. Chloroplatinate (Found: Pt, 43.67. Calculated for $(NH_4)_2PtCl_6$: Pt, 43.96%).

Unchanged alanine (0.05 g.) was recovered from the final residue.

Detection of acetaldehyde. Alanine (1.1375 g., 1/80 mol) was electrolyzed in N H_2SO_4 (120 c.c.) at 35°, bubbling air current between the electrodes in order to expel the volatile substances as quickly as possible. The volatile substances were caught in three washing bottles containing water. C.D.: 2 amp./dm.^{2} Current quantities: 7.203 F./mol. NH_3-N/total N = 47.52%. The solution of volatile substances caught in the washing bottles gave aldehydic reactions and yielded 0.318 g. of acetaldehyde (57.7%, estimated by the bisulphite method). *p*-Nitrophenylhydrazone was precipitated from the solution and recrystallized from dilute alcohol. M.p. 126°. It was identified as acetaldehyde-*p*-nitrophenyhydrazone.

In the same manner, alanine (1/80 mol) was electrolyzed with the current quantities of 6.02 F./mol. The distribution of nitrogen in the electrolyzate: NH_3-N/total N = 47.0%. In this case, the three washing bottles consisted of the one containing water (I) and the others containing dilute alcoholic solution (5%) of dimedon[10] (II, III). Acetaldehyde-*p*-nitrophenylhydrazone (0.04 g.) was obtained from the bottle I, m.p. 120° before and 126° after recrystallization. Acetaldehyde-dimedon was obtained from the bottle II (0.04 g., m.p. 139°) and the bottle III (0.09 g., m.p. 132–134°). The latter was recrystallized from dilute alcohol and it melted at 139°.

II. Electrolytic oxidation of glycine.

Glycine (Kahlbaum) (0.9381 g., 1/80 mol) was dissolved in N H_2SO_4 (30 c.c.) and

(10) Vorländer, *Z. anal. Chem.*, **77** (1929), 241.

electrolyzed under the following conditions. The apparatus is the same as in the case of alanine. Temperature: 99°. Electrodes: lead peroxide anode (2 cm. × 5 cm.), lead cathode (2 cm. × 5 cm.). C.D.: 2 amp./dm.^{2} Current quantities: 6.292 F./mol. The distribution of nitrogen in the electrolyzed solution: NH_3-N/total N = 69.36% (total nitrogen calculated from the glycine).

Volatile acid (*formic acid*). The acid in the distillate driven out during the electrolysis required 4.28 c.c. of 0.1011 N NaOH. The acid in the distillate obtained by the steam distillation required 1.72 c.c. of 0.1011 N NaOH. The total acid amounted to 0.6066 millimol (4.85% to glycine). The acid gave intensely the characteristic reactions of formic acid (the reduction of silver nitrate and mercuric chloride, and the reaction of Hottenroth).

Volatile neutral substance (*formaldehyde*). The above neutralized solution gave the characteristic formaldehyde reaction of fuchsin-sulphurous acid solution containing a little sulphuric acid (Grosse-Bohle). Formaldehyde was estimated by the Romijn's iodine method.[11] Yield 6.2 mg. (16.6% to glycine).

Volatile bases (*ammonia, methylamine, dimethylamine, trimethylamine*).[12] The residue, after the removal of volatile substances by steam distillation, was distilled with an excess of barium hydroxide under reduced pressure. The volatile bases were caught in hydrochloric acid. The very hygroscopic chlorides (1.4 g.) were obtained and treated with absolute alcohol to separate into the soluble and insoluble (0.85 g.) parts. The crystals obtained from the part insoluble in absolute alcohol were identified as ammonium chloride by the behaviour under poralisation microscope and by the analysis of its chloroplatinate (Found: Pt, 43.71. Calculated for $(NH_4)_2PtCl_6$: Pt, 43.96%).

After distilling off alcohol from the part soluble in absolute alcohol, the residual chloride was mixed with sea sand, dried and extracted with hot chloroform. The part insoluble in chloroform was treated with yellow mercuric oxide to make it free from ammonia by the method of François, and then converted into chloroplatinate (0.48 g.), which decomposed at 220°. It was identified as monomethylamine (Found: Pt, 41.56. Calculated for $(CH_3{\cdot}NH_2)_2H_2PtCl_6$: Pt, 41.35%). Monomethylamine-picrolonate was obtained, which decomposed at 244°.

The part soluble in chloroform (dimethyl- and trimethyl-amines) was freed from chloroform, dissolved in water and cooled to 0°, from which a small quantity of crystals of trimethylamine periodide was precipitated by adding iodine–potassium iodide solution. The crystals were dissolved in sodium bisulphite solution, and distilled with steam after an addition of sodium hydroxide solution. The distillate containing trimethylamine required 0.30 c.c. of 0.1065 N H_2SO_4. The mother liquor of precipitate of trimethylamine periodide was distilled with steam after an addition of sodium bisulphite and sodium hydroxide. The distillate containing dimethylamine required 2.80 c.c. of 0.1065 N H_2SO_4. The chloroplatinate decomposed at 206° (Found: Pt, 39.57. Calculated for $[(CH_3)_2NH]_2H_2PtCl_6$: Pt, 39.04%).

Only unchanged glycine was recovered from the final residue.

III. Electrolytic oxidation of valine.

dl-Valine (Fränkel, 0.5855 g., 5 millimols) was electrolyzed in N H_2SO_4 (30 c.c.)

(11) G. Romijn, *Z. anal. Chem.*, **36** (1897), 19.
(12) Abderhalden, "Handbuch der Biologischen Arbeitsmethoden," Abt. I, **7**, 349, Berlin (1925); J. Bertheaume, *Compt. rend.*, **150** (1910), 1063, 1251.

at 99°. Electrodes: lead peroxide anode (4 cm. × 7.5 cm.), lead cathode (4 cm. × 4 cm.). C.D.: 2 amp./dm.^{2} Current quantities: 6.209 F./mol. NH_3-N/total N = 89.3%.

Volatile acid (*isobutyric acid*). The acid required 12.24 c.c. of N/10 NaOH. Yield 27.5% to valine.

Volatile neutral substance (*isobutyraldehyde*). Isobutyraldehyde-*p*-nitrophenylhydrazone (0.3328 g., 32.1% to total valine, 36% to decomposed valine), recrystallized from dilute alcohol gave m.p. 132° (Found: N, 20.33. Calculated for $C_{10}H_{13}N_3O_2$: N, 20.29%).

Volatile base (*ammonia*). Hydrochloride (0.2 g.). Ammonium chloroplatinate (Found: Pt, 43.81. Calculated for $(NH_4)_2PtCl_6$: Pt, 43.96%).

IV. Electrolytic oxidation of leucine.

Leucine (Found: N, 10.50. Calculated for $C_6H_{13}O_2N$: N, 10.69%). Cell: glass cylinder (diameter 7 cm., height 23 cm.) with a rubber stopper which carried two electrodes, a gas delivery tube, a thermometer and a dropping funnel. Electrodes: lead peroxide anode (10 cm. × 16 cm.), nickel cathode (10 cm. × 7 cm.).

Leucine (40 g.) was dissolved in N H_2SO_4 (400 c.c.) and electrolyzed at about 100° in the same manner as in the case of aspartic acid. During the electrolysis a solution of leucine (160 g.) in 4N H_2SO_4 (400 c.c.) was dropped into the cell from a dropping funnel. C.D.: 2 amp./dm.^{2} Current quantities: 6.98 F./mol. 3 volts. The distillate obtained during the electrolysis consisted of oily (83 g.) and aqueous layers. The former consisted almost solely of isovaleraldehyde. The latter was an aqueous solution of isovaleric acid (0.0331 equivalent) together with a little isovaleraldehyde. In the same manner, a comparatively large amount of leucine was electrolyzed, and the product was separated into the following four fractions (A, B, C, D).

(A) Acidic part of oily layer. Oil (3 kg.) was shaken with 2% sodium carbonate solution and separated into acidic and neutral parts. The acidic part was extracted with ether and dried over anhydrous sodium sulphate. After expelling off the ether, the residue was fractionated under reduced pressure as described in Table 1.

Table 1.

Fraction	Boiling point at 26 mm.	Distillate (g.)	Isovaleric acid (%) (determined by titration)	Ag % of the silver salt
1	up to 80°	0.9	—	—
2	80–88°	44.7	100.5	51.80
3	88–89°	25.2	100.2	51.78
4	89–91°	4.4	99.4	51.56
5	91°	0.7	99.4	51.51
		Total 75.9		

Calc. for $C_5H_9O_2Ag$: Ag, 51.63%

Anilides were prepared from the fractions 2 and 3, and recrystallized from dilute alcohol. Both melted at 110–111° (isovaleranilide m.p. 110–111°).

(B) Neutral part of oily layer. The neutral part obtained above was dried over anhydrous sodium sulphate, and fractionated as described in Table 2.

Table 2.

Fraction	Boiling point	Distillate (g.)	Specific gravity (23°)
1	75–90°	318	0.7945
2	90–100°	1592	0.7948
3	100–110°	239	0.8076
4	residue	(297)	0.8157

The greater part of this neutral part was aldehyde. Isovaleraldehyde-*p*-nitrophenylhydrazone (0.3 g.) was prepared from the fraction 1 and recrystallized from chloroform. It melted at 110–111°. The same nitrophenylhydrazone was obtained from the fractions 2 and 3; both melted at 110–111°. Isovaleraldehyde-*p*-nitrophenylhydrazone (Found: N, 19.12 (2), 19.14 (3). Calculated for $C_{11}H_{15}N_3O_2$: N, 19.00%).

As the residue (297 g.) in Table 2 contained 3.91% of acid, it was treated with dilute sodium carbonate solution to remove the acid, then dried and fractionated.

Table 3.

Fraction	Boiling point	Distillate (g.)	Fraction	Boiling point	Distillate (g.)
1	84–89°	0.6	6	129–130°	20.0
2	89–92°	2.7	7	130–132°	2.0
3	92–125°	1.6	8	132–135°	2.1
4	125–128°	28.3		residue	7.6
5	128–129°	38.0			Total 102.9

Fractions 1, 2 and 3 contained isovaleraldehyde. Fractions 4, 5 and 6 are now under investigation.

(C) Acidic part of aqueous layer. Aqueous solution (105 litres) was neutralized with sodium carbonate solution and distilled to remove the neutral part. The sodium salt thus obtained was decomposed with dilute sulphuric acid. The acid was dried and fractionated under reduced pressure.

Table 4.

Fraction	Boiling point at 29.4 mm.	Distillate (g.)	Isovaleric acid (%) (determined by titration)	Ag % of the silver salt
1	37–51°	27.7	—	—
2	51–89°	14.3	86.4	51.86
3	89–92°	202.1	101.1	51.94
4	92–95°	34.2	99.6	51.45

Calc. for $C_5H_9O_2Ag$: Ag, 51.63%

Isovaleranilide was prepared. M.p. 110–111°. The acids lower than isovaleric acid were not found.

(D) Neutral part of aqueous layer. The aqueous layer of the distillate (obtained during electrolysis) was neutralized with sodium carbonate solution and extracted with ether. The ethereal extract was dried as usual, and fractionated after removing the ether.

Table 5.

Fraction	Boiling point	Distillate (g.)	Fraction	Boiling point	Distillate (g.)
1	50–75°	2.1	5	105–115°	0.9
2	75–85°	1.7	6	115–125°	1.7
3	85–95°	35.7	7	125–127°	8.1
4	95–105°	1.3		residue	11.3
					Total 62.8

Fraction 3 gave isovaleraldehyde-*p*-nitrophenylhydrazone, m.p. 110–111° (Found: N, 18.98. Calculated for $C_{11}H_{15}N_3O_2$: N, 19.00%). The main portion of this neutral part consisted of isovaleraldehyde.

Volatile base (ammonia). Ammonium chloroplatinate (Found: Pt, 43.95. Calculated for $(NH_4)_2PtCl_6$: Pt, 43.96%).

In conclusion, the authors express their sincere thanks to Prof. K. Matsubara for kind inspection of this paper.

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The Third Absorption Bands of Co-ordination Compounds. IV. $[Co\,dg_2'\,py\,Cl]$, $[Co(NH_3)_2(NO_2)_2ox]NH_4\cdot H_2O$ and $[Co\,ox_3]K_3\cdot 3.5H_2O$.

By Shin KASHIMOTO and Masahisa KOBAYASHI.

(Received June 23rd, 1937.)

According to Y. Shibata[1] and R. Tsuchida,[2] the third absorption bands of co-ordination compounds in aqueous solutions are due to a pair or pairs of negative radicals co-ordinated in trans positions, and a number of cobaltic complex compounds which have such third absorption bands have been illustrated by those[1][2][3] and the present[2][3][4] authors. The couples of negative radicals hitherto proved to give rise to the third bands may be classified according to their nature: (a) two univalent

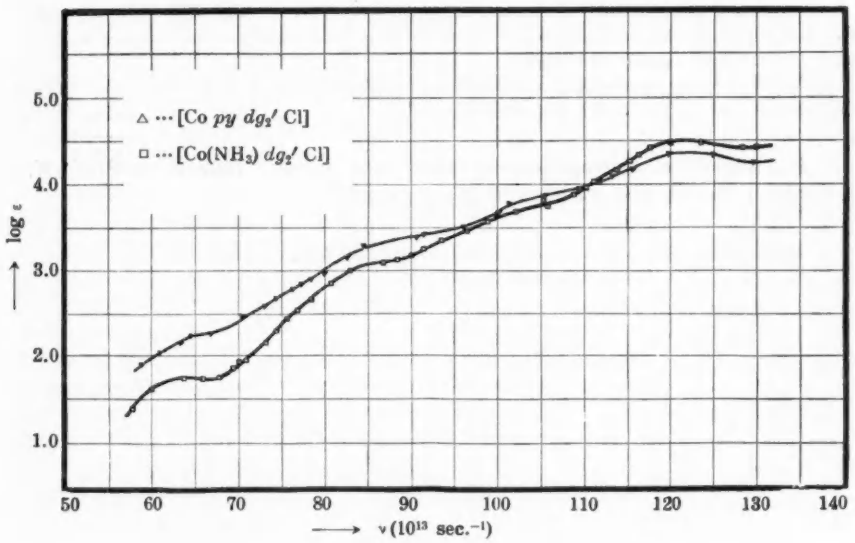

Fig. 1.

(1) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1243.
(2) R. Tsuchida and S. Kashimoto, this Bulletin, **11** (1936), 785.
(3) R. Tsuchida and M. Kobayashi, this Bulletin, **12** (1937), 83.
(4) M. Kobayashi, A. Hagitani, and I. Mita, *J. Chem. Soc. Japan*, **58** (1937), 391.

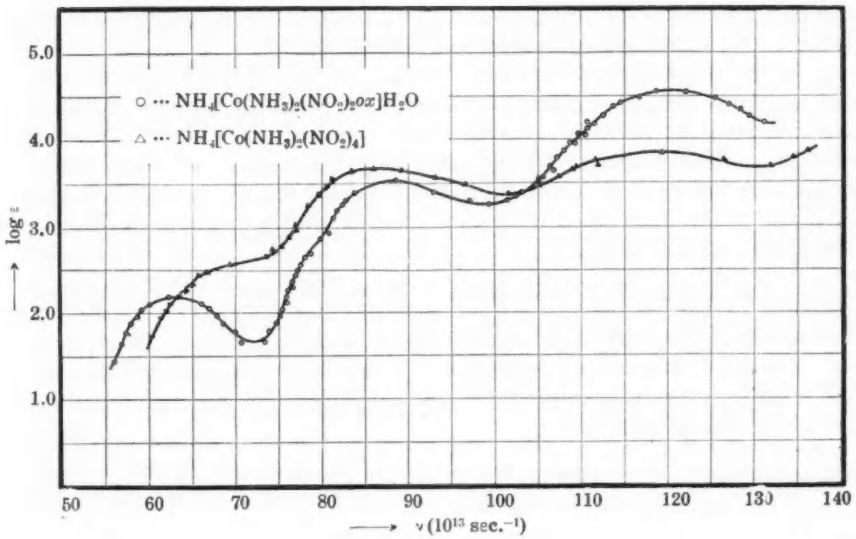
5.0
4.0
3.0
2.0
1.0
log ε
○ ··· NH4[Co(NH3)2(NO2)2ox]H2O
△ ··· NH4[Co(NH3)2(NO2)4]
50
60
70
80
90
100
110
120
130
140
ν (10¹³ sec.⁻¹)

Fig. 2.

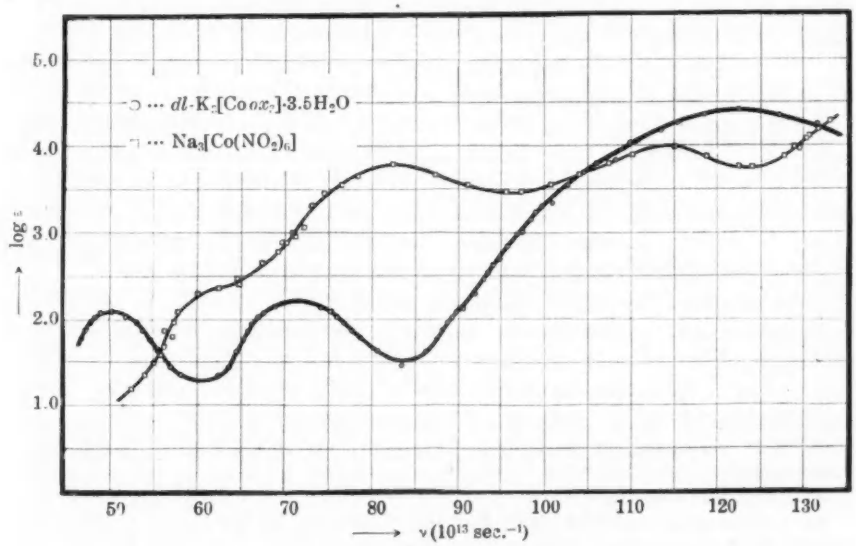
5.0
4.0
3.0
2.0
1.0
log ε
○ ··· dl-K2[Coox2]·3.5H2O
□ ··· Na3[Co(NO2)6]
50
60
70
80
90
100
110
120
130
ν (10¹³ sec.⁻¹)

Fig. 3.

radicals, e.g., NO_2–NO_2, NO_2–Cl and Cl–Cl; and (b) two chelate univalent groups, e.g., dimethylglyoxime–dimethylglyoxime.

In the present paper another example of the class (b) is reported and moreover two other classes have been introduced: (c) one univalent and one bivalent radicals, i.e., NO_2–C_2O_4; and (d) two chelate bivalent radicals coupled with one valence each, i.e., C_2O_4–C_2O_4. In other words, it has been shown that a chelate bivalent radical such as oxalate can also give rise to the third band when it is coupled with a negative radical coordinated in trans position.

$[Co(NH_3)_2(NO_2)_2ox]NH_4 \cdot H_2O$[5] and $[Co\,ox_3]K_3 \cdot 3.5H_2O$[6] were prepared by the methods of Jörgensen and $[Co\,dg'_2\,py\,Cl]$[7], by that of Tschugaeff. The extinction coefficients of these compounds in aqueous solutions were determined for concentrations between 0.01 and 0.002 mol/l. and with varying thicknesses from 0.2 to 50 mm. The absorption curves are given in Fig. 1, 2, and 3.

The authors are indebted to Prof. R. Tsuchida for suggestion and advice on this work.

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Imperial University of Osaka.

(5) S. M. Jörgensen, *Z. anorg. Chem.*, **11** (1896), 416. The symbol *ox* denotes an oxalate radical.

(6) *Ibid.*, **11** (1896), 440.

(7) L. Tschugaeff, *Ber.*, **40** (1907), 3503, 3505. The symbols *dg'* and *py* represent a dimethylglyoxime radical and a pyridine molecule respectively.

Some Cholesterol Derivatives.

By Yoshiyuki URUSHIBARA, Toshio ANDO, Hisakazu ARAKI, and Asaitirô OZAWA.

(Received July 5th, 1937.)

3-Phenyl-cholestadiene and 3-α-Naphthyl-cholestadiene. The reaction mixture of cholestenone (I) (1 mol) and phenyl magnesium bromide (3 mols) as Grignard's reagent was treated with dilute sulphuric acid. The product was freed from diphenyl and unchanged bromobenzene by steam distillation, and recrystallized from a mixture of acetone and methyl alcohol, colourless plates, m.p. 174–5° (corr.), $[\alpha]_D^{29°} = -133°$ (12.0 mg. in 1 c.c. $CHCl_3$ solution, $l = 1$ dm., $\alpha_D^{29°} = -1.60°$), absorption maxima in hexane, 235, 285 mμ. The substance was found to be a 3-phenyl-cholestadiene (III, R = C_6H_5) (Found: C, 89.60, 89.32; H, 11.76, 12.12; molecular weight by Rast's method, 449. Calculated for $C_{33}H_{48}$: C, 89.12; H, 10.88%; molecular weight, 445).(1)

Similarly, from cholestenone and α-naphthyl magnesium bromide a 3-α-naphthyl-cholestadiene (III, R = α-$C_{10}H_7$) was obtained in colourless prisms, m.p. 131–3° (corr.), $[\alpha]_D^{29°} = -49.7°$ (14.3 mg. in 1 c.c. $CHCl_3$ solution, l=1 dm., $\alpha_D^{29°} = -0.71°$), absorption maximum in hexane, 283 mμ (Found: C, 90.57, 90.95; H, 10.51, 10.51; molecular weight by Rast's method, 501. Calculated for $C_{37}H_{50}$: C, 89.80; H, 10.20%; molecular weight, 495).(1)

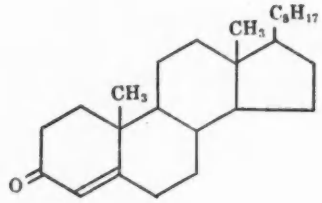
These cholestadiene derivatives distil unchanged in high vacuum. In Rosenheim test the phenyl compound gives a violetish blue colouration, while the α-naphthyl compound a greenish blue colouration. No exact evidence is yet available for the positions (as accepted in formula III) of the two double bonds in the cholestadiene part of these compounds, and the alternative formula III′ can not totally be excluded.

On evaporating a benzene solution (orange red) containing equi-molecular amounts of the α-naphthyl-cholestadiene and picric acid a picrate melting at 161–3° (corr.) was obtained in orange red crystals. The fusion curve of the two compounds also shows the existence of a molecular compound (1:1), giving a maximum (161°) at the molecular ratio 1:1(2).

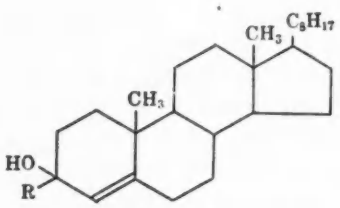
Tertiary alcohols as represented by formula II are considered to be the primary products of the Grignard reactions described above. But they

(1) Owing to the sultry weather of the rainy season when the experiments were carried out, the data of micro-analyses are not quite satisfactory.

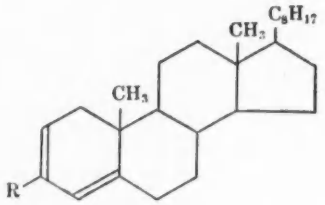
(2) The fusion curve was obtained by Dr. C. Shinomiya, to whom the authors' thanks are due.



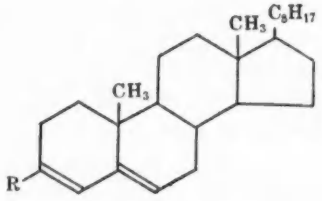
I



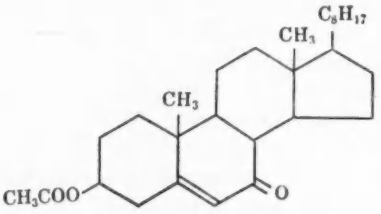
II



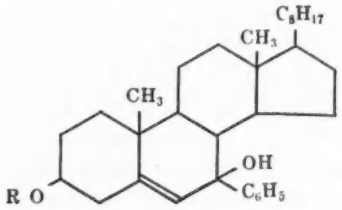
III



III′



IV



V

could not be isolated and dehydration took place readily under the conditions of the experiments, giving rise to the cholestadiene derivatives (III). Such easy dehydration of tertiary alcohols is sometimes the case in Grignard reactions. To give an example in the sterol series, 7-methylene-cholesterol is formed in the reaction of methyl magnesium iodide with 7-keto-cholesteryl acetate[3][4]. The ready formation of the cholestadiene derivatives (III) may be quite natural in view of the fact that the tertiary alcohols (II) are 3-aryl derivatives of either allocholesterol or *epi*-allocholesterol, because both

(3) B. Bann, I. M. Heilbron, and F. S. Spring, *J. Chem. Soc.*, **1936**, 1274.
(4) S. Weinhouse and M. S. Kharasch, *J. Org. Chem.*, **1** (1936-7), 490.

allocholesterol and *epi*-allocholesterol lose easily water[5], and the tertiary nature of the hydroxyl group would facilitate dehydration.

7-Hydroxy-7-phenyl-cholesterol and Its Benzoate. Action of phenyl magnesium bromide (4 mols) on 7-keto-cholesteryl acetate (IV) (1 mol), followed by decomposition by aqueous ammonium chloride and recrystallization from benzene, yielded 7-hydroxy-7-phenyl-cholesterol (V, R = H) in colourless needles, m.p. 150.5–151.5° (corr.), $[\alpha]_D^{29°} = -137°$ (18.1 mg. in 1 c.c. $CHCl_3$ solution, $l = 1$ dm., $\alpha_D^{29°} = -2.48°$). Its monobenzoate (V, R = C_6H_5CO), prepared by the action of benzoyl chloride and pyridine, was recrystallized from acetone in colourless needles, m.p. 205.5–206° (corr.), $[\alpha]_D^{28°} = -79.1°$ (21.5 mg. in 1 c.c. $CHCl_3$ solution, $l = 1$ dm., $\alpha_D^{29°} = -1.70°$) (Found : C, 82.31 ; H, 10.12. Calculated for $C_{40}H_{54}O_3$: C, 82.41 ; H, 9.35%).

When the benzoate was heated in high vacuum (0.0005 mm.), a small amount of benzoic acid sublimed (about 200°), but the most part (90%) of the material distilled unchanged (up to 280°). On heating the benzoate under a higher pressure (200–250°, 0.18 mm.), a greater amount of benzoic acid sublimed, but from the residue the unchanged material only was isolated. Thus it seems that 7-hydroxy-7-phenyl-cholesteryl benzoate loses practically neither water nor benzoic acid on heating in vacuum. S. Weinhouse and M.S. Kharasch[4] also have described 7-hydroxy-7-phenyl-cholesterol, which they could not dehydrate: Informations so far obtained show that elimination of water from the tertiary hydroxyl group at carbon atom 7 in cholesterol derivatives is either effected with the formation of an exocyclic double linkage or not effected at all[3][4][6]. 7-Hydroxy-7-phenyl-cholesterol can not afford the formation of an exocyclic double linkage, and must necessarily resist dehydration.

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The Effect of Oxygen on the Addition of Bromine to Cinnamic Acid in Carbon Tetrachloride.

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The inhibiting effect of oxygen on the addition of bromine to cinnamic acid in carbon tetrachloride was first observed by W. H. Bauer and F. Daniels.[1] They found that bromine and cinnamic acid combine rapidly in the dark at room temperature when dissolved oxygen has been removed from the solution, and when the oxygen has not been removed, the reaction is very slow in the dark, but it proceeds rapidly in the light.

The present paper records the results of somewhat quantitative experiments on the effect of oxygen on the addition of bromine to cinnamic acid in carbon tetrachloride. Special care was taken in purifying the materials, viz. cinnamic acid, bromine, and carbon tetrachloride, and in excluding moisture. A solution of 1 millimol (0.1480 g.) of cinnamic acid in 30 c.c. of carbon tetrachloride was placed in a reaction tube of Pyrex glass with a capacity of 140 c.c. A sealed small glass bulb containing a slight excess of bromine was slipped into the tube. The tube was cooled in liquid air, evacuated, and sealed off with or without admission of oxygen. The contents were melted and mixed well by shaking. The breaking of the bromine bulb usually took place on freezing the contents of the reaction tube in liquid air, otherwise effected by shaking. The tube was then placed in the dark at room temperature for 22 hours. An excess of aqueous potassium iodide was added to the reaction mixture, and the liberated iodine was titrated with N/10 sodium thiosulphate. The extent of addition (in percentage to the cinnamic acid used) was determined from the amount of bromine consumed. The results are summarized in Table 1.

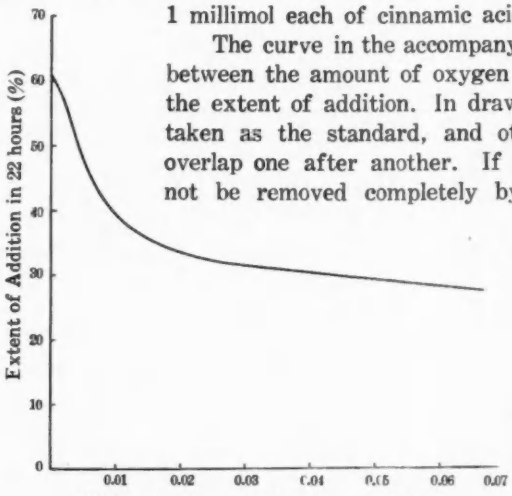
Each one group of experiments were carried out simultaneously, and thus under the same conditions. According to the measurements of the solubility of oxygen in carbon tetrachloride by J. Horiuti[2] the ratio of the concentration of oxygen dissolved in carbon tetrachloride to that in the gaseous phase is 0.3 at ordinary temperature. The partial pressure of oxygen in the tube at respective temperature, and the amount of oxygen

(1) *J. Am. Chem. Soc.*, **56** (1934). 2014.
(2) *Sci. Papers Inst. Phys. Chem. Research* (Tokyo), **17** (1931), 213.

Table 1.

Group of exp.	No. of exp.	Bromine (g.)	Oxygen						Extent of addition (%)
			Vol. (c.c.)	Temp. (°C.)	Pres. (mm.)	Vol. n.p.t. (c.c.)	Partial pressure in the tube (mm.)	Amount dissolved in CCl_4 solution (millimol)	
I	1	0.1758	0			0	0	0	60.6
	2	0.1778	0.5	22	757.8	0.46	3.2	0.0016	57.8
	3	0.1800	1.0	22	757.8	0.92	6.4	0.0031	53.4
	4	0.1849	2.0	22	757.8	1.85	13	0.0062	44.9
II	5	0.1854	0			0	0	0	56.6
	6	0.2011	2.0	21	757.0	1.85	13	0.0062	40.7
	7	0.2004	5.0	21	757.0	4.63	32	0.016	31.2
III	8	0.2170	5.0	21	756.7	4.62	32	0.016	32.4
	9	0.2151	10.0	21	756.7	9.25	64	0.031	28.5
IV	10	0.2035	10.0	20	757.3	9.28	64	0.031	33.1
	11	0.2033	20.0	20	757.3	18.57	127	0.063	29.4

dissolved in the carbon tetrachloride solution were calculated on the assumption that this ratio holds in the carbon tetrachloride solution containing 1 millimol each of cinnamic acid and bromine in 30 c.c.



Milli-mols of Oxygen in 30 c.c. CCl_4 Solution containing 1 millimol of Cinnamic acid.

The curve in the accompanying figure shows the relation between the amount of oxygen present in the solution and the extent of addition. In drawing this curve Group I was taken as the standard, and others were shifted so as to overlap one after another. If the dissolved oxygen could not be removed completely by the process of evacuation under cooling in liquid air, as it seems possible from the observation of Bauer and Daniels that the addition was so rapid in absence of oxygen that the rate of reaction could not be measured conveniently, the ordinate must be displaced as much to the left.

In Table 2 addition in vacuum with 1 millimol of

cinnamic acid in 30 c.c. of carbon tetrachloride (exp. 12 and 14) is compared with that on a half scale but in a tube of the same dimensions (exp. 13 and 15). There is no significant difference in the extent of addition. The last group of experiments recorded in Table 3 shows that the shaking of the tube during the reaction had practically no influence on the extent of addition. (The greater values of the extent of addition for the last group of experiments were probably caused by the higher room temperature.) These results seem to indicate that the addition of bromine to cinnamic acid in carbon tetrachloride under the conditions as described above is a homogeneous reaction.

Table 2. (Reaction time, 22 hours.)

Group of exp.	No. of exp.	Cinnamic acid (millimol)	CCl_4 (c.c.)	Bromine (g.)	Extent of addition (%)
V	12	1	30	0.1924	61.8
	13	0.5	15	0.0807	56.7
VI	14	1	30	0.1912	62.1
	15	0.5	15	0.0790	65.5

Table 3. (Cinnamic acid, 1 millimol; CCl_4, 30 c.c.; Reaction time, 22 hours.)

Group of exp.	No. of exp.	Bromine	Extent of addition (%)	Remarks
VII	16	0.1779	75.72	The tube was shaken during the reaction.
	17	0.1768	75.28	The tube was not shaken

No detectable peroxide was formed from cinnamic acid and oxygen in carbon tetrachloride even in bright diffused light. This fact makes it very probable that the effect of oxygen on the addition of bromine to cinnamic acid in carbon tetrachloride is caused by the action of molecular oxygen.

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